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(54) PROCESS FOR THE MANUFACTURE OF 4-HYDROXY-3-NITROBENZOIC ACID

5 (71) We, HOECHST AKTIENGESELLSCHAFT, formerly Farbwerke Hoechst Aktiengesellschaft, vormals Meister Lucius & Brüning, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt (Main) 80, Postfach 80 0 3 20, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention provides an improved process for the preparation of 4-hydroxy-3-nitrobenzoic acid by nitration of 4-hydroxybenzoic acid with nitric acid.

15 4-hydroxy-3-nitrobenzoic acid is a valuable intermediate product for the preparation of dyestuffs, optical brighteners, heat-resistant plastics and fibres and pesticides. It can be prepared by nitration of 4-hydroxybenzoic acid with dilute nitric acid at an elevated temperature (cf. Berichte der Deutschen Chemischen Gesellschaft 20, 408 (1887) and 29, 1756 (1896)), with dilute nitric acid in the presence of sodium nitrite at 20 55—60°C (cf. J. Soc. Chem. Ind. 65, 211 (1945)), with fuming nitric acid in glacial acetic acid at 30—40°C (cf. J. Chem. Soc. 25 1935, 200) or with concentrated nitric acid in chloroform (cf. Monatsheft für Chemie 68, 258 (1936)).

30 However, the 4-hydroxy-3-nitrobenzoic acid obtained according to these processes in varying yield always contains by-products so that a subsequent purification is inevitable.

35 This invention is based on the observation that 4-hydroxy-3-nitrobenzoic acid can be obtained by nitration of 4-hydroxybenzoic acid with nitric acid in high yield and purity, by carrying out the nitration at from 20 to 40°C with 25 to 35% by weight nitric acid with the addition of catalytic amounts of an inorganic nitrite.

40 45 The process is advantageously carried out in such a manner that an aqueous alkaline solution of 4-hydroxybenzoic acid, (as ob-

tained for example by dissolution of hydroxybenzoic acid in a double molar amount of an aqueous alkali metal hydroxide solution or particularly after treating with water the corresponding product obtained from a potassium phenolate carboxylation) is mixed with such an amount of concentrated, for example 62% by weight nitric acid that a suspension of finely divided free 4-hydroxybenzoic acid in 25 to 35% by weight nitric acid is formed which is stirred, after addition of a catalytical amount of a nitrate, for example an alkali metal nitrite for example sodium or potassium nitrite, for several hours at temperatures of from 20 to 40°C. The suspension of the 4-hydroxy-3-nitrobenzoic acid obtained is then filtered, washed with water and optionally dried.

50 The use of finely divided 4-hydroxybenzoic acid, which can also be obtained by grinding or dispersing, preferably in the presence of water or diluted nitric acid, ensures in any case the preparation of 4-hydroxy-3-nitrobenzoic acid free from 4-hydroxybenzoic acid which is not the case with other methods. Due to the low nitration temperatures, by-products and metabolons resulting from decarboxylation or further nitration are not formed in the process of the invention. Therefore, the 4-hydroxy-3-nitrobenzoic acid obtained by the process may be used directly for further reactions, for example, by esterification with lower alcohols it may be converted into 4-hydroxy-3-nitrobenzoic acid alkyl esters or it may be reduced to 3-amino-4-hydroxybenzoic acid.

55 60 65 70 75 80 85 90 The following Example illustrates the process of the invention. Parts are by weight.

EXAMPLE:

1300 parts of 62% by weight nitric acid were poured while stirring into a solution of 4-hydroxybenzoic acid dipotassium salt (corresponding to 159 parts of free 4-hydroxybenzoic acid) in 600 parts of water, whereby the 4-hydroxybenzoic acid was pre-

precipitated in a finely divided form. The temperature of the reaction mixture was not allowed to exceed 35°C.

After addition of small amounts of sodium nitrite the nitration began. This could be seen by the increase in temperature which was maintained at 36 to 38°C by slight cooling. After the exothermal reaction which lasted for 2 to 3 hours was finished, the whole was diluted with 2500 parts of water at 20°C, stirring was continued for 1 hour at 20—30°C; the mixture was suction-filtered, washed free from nitrate and dried. 170 parts of 4-hydroxy-3-nitrobenzoic acid having a melting point of 178°C were obtained, wherein no isomers, polynitro compounds and decarboxylation products could be detected by chromatography and which was very suitable as starting compound without any further purification for the preparation of other compounds for example esterification to form 4-hydroxy-3-nitrobenzoic acid methyl ester.

Instead of an aqueous alkali metal salt solution of the 4-hydroxybenzoic acid, the product obtained for example by carboxylation of potassium phenolate according to Kolbe-Schmitt and dissolving out the reaction product with water, a dispersion of the corresponding parts of free 4-hydroxybenzoic acid and 1200 parts of 30% by weight nitric acid may be used, as obtained

for example by grinding the two components together. The reaction was then carried out as indicated in the Example above, the 4-hydroxy-3-nitrobenzoic acid being obtained in practically the same yield and quality.

WHAT WE CLAIM IS:—

1. A process for the manufacture of 4-hydroxy-3-nitrobenzoic acid by nitration of 4-hydroxybenzoic acid with nitric acid, wherein nitration is carried out from 20 to 40°C with 25 to 35% by weight nitric acid and the addition of a catalytic amount of an inorganic nitrite.

2. A process as claimed in claim 1, wherein finely divided 4-hydroxybenzoic acid is used.

3. A process as claimed in claim 1 or 2, wherein an alkali metal nitrite is used.

4. A process as claimed in claim 1 conducted substantially as described and exemplified herein.

5. 4-Hydroxy-3-nitrobenzoic acid whenever obtained by a process claimed in any one of claims 1 to 4.

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